Journal of Molecular Liquids 264 (2018) 1–8

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

B_{40} and $M@B_{40}$ (M=Li and Ba) fullerenes as potential molecular sensors for acetone detection: A first-principles study

Yongliang Yong [a,b,*], Xiangying Su [a,b], Yanmin Kuang [c], Xiaohong Li [a,b], Zhansheng Lu [d]

[a] College of Physics and Engineering, Henan University of Science and Technology, Luoyang 471023, China
[b] Henan Key Laboratory of Photoelectric Energy Storage Materials and Applications, Henan University of Science and Technology, Luoyang 471023, China
[c] Institute of Photobiophysics, School of Physics and Electronics, Henan University, Kaifeng 475004, China
[d] College of Physics and Materials Science, Henan Normal University, Xinxiang 453007, China

ARTICLE INFO

Article history:
Received 13 January 2018
Received in revised form 14 March 2018
Accepted 10 May 2018
Available online xxxx

Keywords:
B_{40} fullerenes
$M@B_{40}$ (M=Li and Ba)
Acetone sensor
Gas sensing properties
DFT calculations

ABSTRACT

The adsorption of acetone on B_{40} and $M@B_{40}$ (M=Li and Ba) has been studied by means of density functional theory calculations. It is demonstrated that the acetone molecule can easily chemisorb on the B_{40} and $M@B_{40}$ from physisorption states with very small energy barriers. The adsorption strength is moderate and the charge transfer between acetone and B_{40} (or $M@B_{40}$) is apparent. Moreover, the M-doping can slightly enhance the adsorption strength. The electric conductivity of B_{40} (or $M@B_{40}$) changes obviously due to the acetone adsorption. The recovery times for B_{40} or $M@B_{40}$, in particular for B_{40} at $T = 300$ K are quite short, very different from NH_3 or NO_2 adsorbed on B_{40}. Our results suggest that the B_{40} and $M@B_{40}$ (M=Li and Ba) can be viewed as high sensitive molecular sensors for acetone detection with short recovery time.

1. Introduction

In the last few decades air pollution, both indoors and outdoors, has become an important and intractable issue, endangering human health and impeding sustainable development in turn. Development of gas sensors to detect pollutant gases, even at a very low concentration, is therefore a highly critical area of research [1–5]. Acetone, a hazardous and widely used chemical gas in industrial processes, can have a narcotic effect on central nervous system and cause skin and eyes irritation, mood swings, and nausea [6–9]. In particular, acetone in human breath exhaust is one of the commonly considered biomarkers for type-I as well as type-II diabetes [6,7]. Therefore, it is of great significance and interesting to develop acetone gas sensor with high performance for environmental monitoring and human health protection.

Nowadays, nanocluster-based gas sensors have been viewed as one of the most promising candidates for detecting gases [10–27], because nanoclusters offer many advantages such as higher surface-to-volume ratio and more surface-active sites. Recently, after the successful discovery of B_{40} fullerene [28], it has been investigated extensively both theoretically and experimentally [29–40]. The most stable B_{40} fullerene with D_{2d} point-group symmetry consists of interwoven double chains with two hexagons at the top and bottom, and four heptagons in the side surface. Furthermore, since metal encapsulation is an effective way to modify the chemical bonding and occupancy of energy level of nanoclusters, which would thus change their physical-co-chemical and thermodynamic properties, the structural stability and electronic properties of B_{40} fullerene have been tuned by doping with various metal species [36–40] to extend the potential applications in nanoboron chemistry. So far, the B_{40} fullerene has been used in many applications such as Li-ion batteries [41] and hydrogen storage [42–45], and in particular because of its cage structure, which offers a large surface-to-volume ratio, it has been viewed as a promising gas sensor to detect harmful gases such as NH_3, CO and NO [24–27]. Recently, Lin et al. has investigated the adsorption of NH_3, N_2, H_2 and CH_4 molecules on B_{40} fullerene using density functional theory (DFT) and the non-equilibrium Green's function (NEGF) method, and their results have shown that B_{40} fullerene can be used as a single molecular gas sensor to detect NH_3 from non-polar gas molecules at low bias [24]. This conclusion has been further confirmed by Moradi and co-workers [26]. Furthermore, B_{40} fullerene has been predicted to be a good CO and NO sensor from a first-principles study [28]. However, to the best of our knowledge, there is no study relating the adsorption of acetone on B_{40} fullerene to realize the gas sensing properties of B_{40}-based acetone sensors.

In this study, to fully exploit the possibilities of the B_{40} fullerene as a molecular sensor for acetone detection, we present a first-principles study based on DFT to precisely describe the adsorption behaviour and electronic properties of acetone (CH_3COCH_3) on the B_{40} fullerene without and with single metal encapsulation. We investigate the adsorption energy, adsorption sites, charge transfer between acetone

---

* Corresponding author.
E-mail address: ylyong@haust.edu.cn (Y. Yong).

https://doi.org/10.1016/j.molliq.2018.05.046

and (endohedral) B_{40} fullerene, the changes of electronic properties due to the adsorption, and the influence of metal encapsulation on the gas sensing properties in detail. Our results show that B_{40} and M@B_{40} (M═Li and Ba) are promising candidates for acetone sensors with high performance, such as high sensitivity and selectivity and quite short recovery time.

2. Computational details

The spin-polarized electronic calculations are performed within the DFT-PBE [46] computational scheme employing with van der Waals correction proposed by Tkatchenko and Scheffler method [47], as implemented in the DMol^3 package (Accelyrs Inc.) [48,49]. The electron ion-core interactions are represented by density-functional semi-core pseudopotentials fitted to all-electron relativistic DFT results [50] and standard DNP basis sets. A convergence criterion of 10^{-6} a.u. on the energy and electron density is used in the self-consistent field calculations, and meanwhile convergence criterions of 10^{-3} a.u. on the gradient and displacement and 10^{-5} a.u. on the total energy are set in geometrical optimization. The geometric parameters are optimized without symmetry constraints. The charge distribution of the considered systems and the charge transfer between B_{40} (or M@B_{40}) and acetone is analyzed based on Hirshfeld analysis [51]. The reliability and accuracy of the DFT-PBE method used here to investigate the structures and electronic properties of borospherene-based materials has been confirmed by previous studies [for example, see Refs. 24, 28, 32, 36, 30, 43, 44].

To further discuss the adsorption behaviour of acetone on the B_{40} and M@B_{40}, transition state geometries are firstly searched by using the complete linear/quadratic synchronous transit (LST/QST) method [52], and then fully optimized within the DFT-PBE level. All transition-state structures are confirmed by harmonic vibrational frequency calculations, which would have only one imaginary frequency along the reaction process.

The adsorption energy (E_a), which can be used to evaluate the adsorption strength of acetone on B_{40} without and with metal-doping, can be defined as.

$$E_a = E_{system} - E_{boron} - E_{acetone} \quad (1)$$

where E_{system}, E_{boron} and $E_{acetone}$ represents the total energy with full relaxation for the acetone adsorbed on the (endohedral) B_{40} fullerene, the corresponding (endohedral) B_{40} fullerene, and the pristine single acetone molecule, respectively.

3. Results and discussion

3.1. Adsorption of acetone on the pure B_{40} fullerene

To obtain the most stable configuration of acetone adsorbed on B_{40}, we have set up all possible initial structures by considering the following issues: (*i*) The adsorption sites on B_{40} fullerene (including top, bridge and hollow sites). Since the B_{40} fullerene has a high symmetry (D_{2d}), there are only six different kinds of boron atoms, which can be viewed as the top sites [25]. The B—B bonds can be viewed as the bridge sites, and the centers of triangles, heptagons and hexagons are regarded as the hollow sites. (*ii*) We mainly considered the carbonyl (C═O) active site of the acetone molecule to bond with the B_{40} fullerene. After relaxation all of the initial structures, we obtained the most stable and some low-lying energy configurations, which are presented in Fig. 1, and the main calculated results are listed in Table 1. The most stable one as shown in Fig. 1a, in which the O atom of the acetone is bonded with one B atom with the bond length of 1.55 Å, has an adsorption energy of −0.681 eV. These results indicate that the acetone is chemisorbed on the B_{40}. The average distance of B—B bonds, where one B atom is bonded with the O atom of acetone, is enlarged from the 1.63 Å in pure B_{40} to 1.71 Å, however, the others do not change obviously. Meanwhile, the C—O bond length enlarges from 1.22 Å in isolated molecule to 1.26 Å, while the average C—C bond length decreases from 1.52 Å in isolated acetone to 1.48 Å. The angle of the O—C—C, where the last C atom is closer to the B_{40} fullerene (see Fig. 1a), increases from 121.6° in isolated state to 124.0°, in the contrary, the angle of the O—C—C, where the last C atom is away from the B_{40} fullerene, decreases from 121.6° in isolated state to 119.4°. The C—C—C angle enlarges from 116.7° to 119.4°. These results indicate that the adsorption induces some obvious deformation on the acetone molecule but only small deformation on the around area of adsorption site in B_{40}. The second stable configuration as shown in Fig. 2b, which is higher by 0.168 eV in energy than the most stable one, has an adsorption energy of −0.513 eV. It is found that the difference between the most and second stable ones is just reflected in the adsorption site. The B—O bond length in the second stable one is 1.62 Å, which is a little larger than that in the case of the most stable configuration. It can be found from the Hirshfeld analysis, there is an apparent charge transfer, which is more than 0.35 e, from the B_{40} to the acetone molecule in chemisorbed configurations, indicating the acetone servers as an acceptor. The energy gap between the highest occupied-(HOMO) and the lowest unoccupied-(LUMO) molecular orbital of the pure B_{40} is 1.770 eV via our DFT-PBE calculations. It is well known that the DFT-

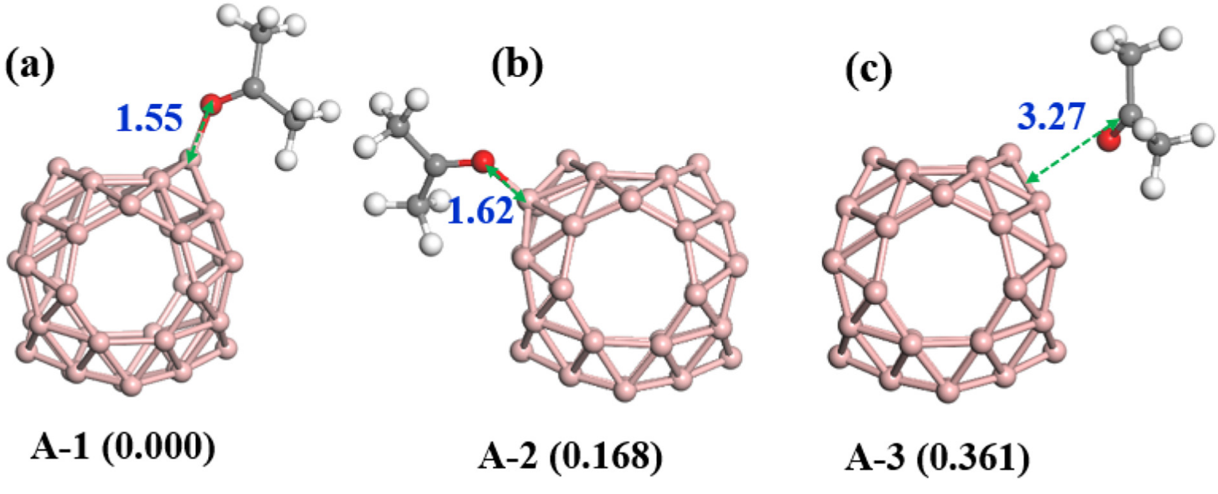

Fig. 1. Optimized structures of acetone adsorbed on the B_{40} fullerene. Isomer structures are labeled as A-*n* ($n = 1, 2, 3$) in order of decreasing stability. Values in parentheses are relative energy in eV with respect to the most stable one (A-1). White, gray, red and pink balls are H, C, O and B atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)